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# LIQUID-PHASE FREE-RADICAL ISOMERIZATION OF CYCLIC ACETALS

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V. S. Martem'yanov, and D. L. Rakhmankulov

UDC 547.729'841 541.515:542.952.1

1,3-Dioxacyclanes are converted to esters in the presence of di-tert-butyl peroxide. The reaction is described by the kinetic equation of an unbranched chain reaction with quadratic chain termination. It is shown that five-membered acetals are more reactive than seven- and six-membered acetals. The introduction of hydrocarbon groups in the 2 position of the ring increases the reactivity. It is concluded that the primary site of attack by the alkyl radical is the methylene or methylidyne group adjacent to the two heteroatoms.

It has previously been shown [1] that 1,3-dioxane is converted to the isomeric propyl formate in the presence of di-tert-butyl peroxide (DTB) via a mechanism involving an unbranched chain reaction.

To study the effect of the ring size and the nature of the substituents on this reaction, we investigated the kinetics of the liquid-phase free-radical isomerization of a number of 1,3-dioxacyclanes.

Cyclic acetals I-VI are converted to the isomeric esters at rate $W_{est}$ during which the $W_{est}/\sqrt{W_{alc}}$ ratio ($W_{alc}$ is the rate of formation of tert-butyl alcohol, which reflects the rate of initiation) remains satisfactorily constant over the range of change in DTB concentrations from 0.05 to 0.70 mole/liter (Table 1). From this it follows that the esters are formed via an unbranched radical-chain mechanism with quadratic chain termination.

The rate of formation of the esters increases linearly as the substrate concentration increases (Fig. 1), and this indicates participation of one acetal molecule in the rate-

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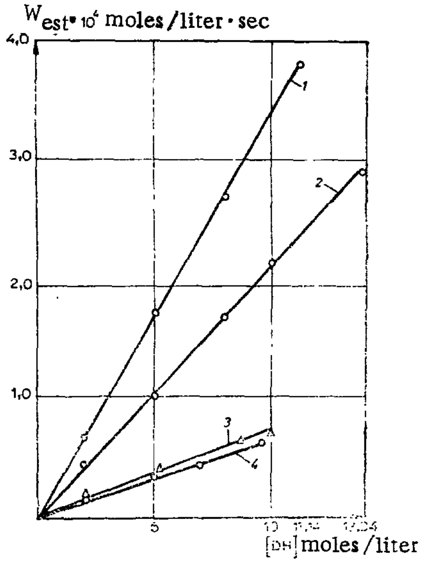


Fig. 1

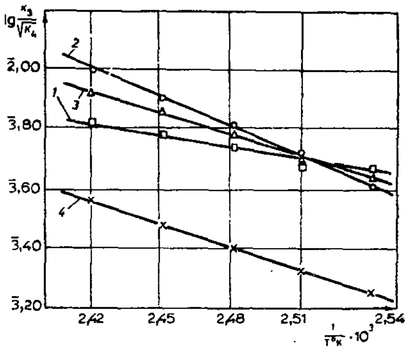


Fig. 2

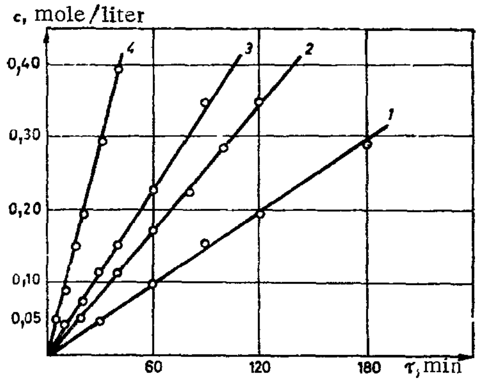


Fig. 3

Fig. 1. Dependence of the initial rate of formation of the esters ($W_{est}$) on the acetal concentration [DH] in benzene at 130°C (DTB = 0.3 mole/liter): 1) 2-methyl-1,3-dioxolane (II); 2) 1,3-dioxolane I; 3) 1,3-dioxepane (VI); 4) 2-methyl-1,3-dioxane (V).

Fig. 2. Dependence of $k_3/\sqrt{k_4}$ on 1/T: 1) I; 2) II; 3) III; 4) IV.

Fig. 3. Kinetics of the accumulation of butyl formate: 1) I, 120°C; 2) II, 125°; 3) III, 130°; 4) IV, 140° ([1,3-dioxepane] = 9.96 moles/liter, [DTB] = 0.3 mole/liter).

determining step. The lines that express the dependence of the rate of accumulation of the esters on the concentration of 1,3-dioxacyclanes I, II, V, and VI pass through the origin; it hence follows that rearrangement of the cyclic radical to a linear radical is not the rate-determining step in the formation of the ester.

The experimental results confirm that 1,3-dioxacyclanes I-VI are isomerized in accordance with the previously proposed mechanism [1] (compare with the mechanism shown below) and that its rate is described by the equation

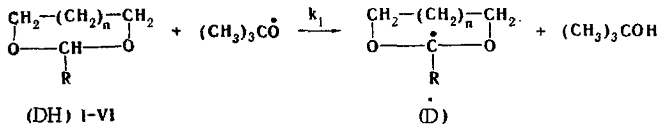
$$W_{est} = k_3/\sqrt{k_4} \cdot [DH] \cdot \sqrt{k_i [DTB]}.$$

Disproportionation of the ester radicals (E) via reaction (4), according to the published data, does not have a substantial effect on the formation of the ester (EH) at 120-145° [2]. It was shown by special experiments that no more than 3% of the tert-butoxyl radicals undergo decomposition to acetone in the pure I-VI preparations even at 140°; this is in good agreement with the known data for 1,3-dioxacyclanes [2], and we can therefore assume, without too much error, that

$$k_i \cdot [DTB] = 0.5 \cdot W_{alc}.$$

A study of the dependence of $W_{est}$ and $W_{alc}$ on the temperature (it is presented in Arrhenius coordinates in Fig. 2) has made it possible to determine the effective activation energy and calculate the preexponential factor.

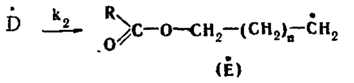
$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{k_i} 2(CH_3)_3C\dot{O} \qquad (0)$$



$$DH + (CH_3)_3C\dot{O} \xrightarrow{k_1} \dot{D} + (CH_3)_3COH \qquad (1)$$

(DH) I-VI

(Ḋ)



$$\dot{D} \xrightarrow{k_2} R\!-\!C(=O)\!-\!O\!-\!CH_2\!-\!(CH_2)_n\!-\!\dot{C}H_2 \qquad (2)$$

(Ė)

TABLE 1. Dependence of the Initial Rate of Accumulation of Ester ($W_{est}$) and tert-Butyl Alcohol ($W_{alc}$) on the di-tert-Butyl Peroxide Concentration (T = 130°C)

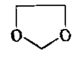
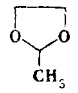
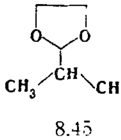
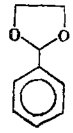
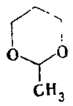
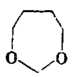
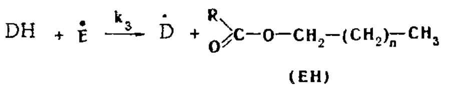
| Compound | Acetal, mole/liter | DTB, mole/liter | $W_{est}\cdot10^4$ mole/liter·sec | $W_{alc}\cdot10^4$ mole/liter·sec | Chain length $\nu = W_{est}/W_{alc}$ | $(W_{est}/\sqrt{W_{alc}})\cdot10^2$ mole/liter$^{1/2}$ sec$^{1/2}$ | $(k_3/\sqrt{k_4})\cdot10^3$ liter/mole·sec$^{1/2}$ |
|---|---|---|---|---|---|---|---|
| I |  | 0,05 | 0,94 | 0,04 | 23,5 | 4,70 | 5,92<br>±0.20 |
| | | 0,10 | 1,60 | 0,08 | 18,9 | 5,49 | |
| | | 0,20/ | 2,27 | 0.17 | 13,4 | 5.51 | |
| | | 0,30 | 3,81 | 0,26 | 10,8 | 5,50 | |
| | | 0,40 | 3,54 | 0,37 | 9,6 | 5.50 | |
| | 13,94 | 0,70 | 4.45 | 0.60 | 7,4 | 5,74 | |
| II |  | 0,05 | 1,25 | 0,07 | 18.1 | 4,76 | 7,00<br>±0.25 |
| | | 0,07 | 1,73 | 0,08 | 10.8 | 6,00 | |
| | | 0,10 | 2,39 | 0,16 | 15,4 | 6,07 | |
| | | 0.20 | 3,51 | 0,38 | 9,3 | 5,70 | |
| | | 0,30 | 3,81 | 0,45 | 8,4 | 5,67 | |
| | | 0.50 | 4,77 | 0,69 | 6,9 | 5.72 | |
| | | 0.85 | 6.11 | 1,22 | 5.0 | 5,53 | |
| | 11,14 | 1,00 | 6,61 | 1.47 | 4.5 | 5,45 | |
| III |  | 0,1 | 1,06 | 0,07 | 15.3 | 4,02 | 6,73<br>±0,05 |
| | | 0,2 | 1.31 | 0,12 | 11,5 | 4,03 | |
| | | 0,3 | 1,78 | 0,19 | 9,1 | 4,03 | |
| | | 0,4 | 2,01 | 0,25 | 8.1 | 4,04 | |
| | | 0,6 | 2,54 | 0,39 | 6,5 | 4,07 | |
| | 8.45 | 1,0 | 3.29 | 0,65 | 5,0 | 4,07 | |
| IV |  | 0,05 | 0,36 | 0,01 | 36,0 | 3,78 | 8,06<br>±0,10 |
| | | 0,10 | 0.60 | 0,03 | 20,0 | 3,73 | |
| | | 0,20 | 0,76 | 0,04 | 10.0 | 3,71 | |
| | | 0,30 | 1.05 | 0.08 | 13,1 | 3,71 | |
| | | 0,40 | 1,11 | 0.09 | 12,4 | 3,71 | |
| | 6.53 | 0,70 | 1.45 | 0.15 | 9,7 | 3,70 | |
| V |  | 0,05 | 0.19 | 0,03 | 6,1 | 1,10 | 1.34<br>±0.10 |
| | | 0,07 | 0,24 | 0.05 | 5,3 | 1,12 | |
| | | 0,10 | 0,36 | 0,08 | 4.5 | 1.27 | |
| | | 0,20 | 0,53 | 0,15 | 3.6 | 1,38 | |
| | | 0,30 | 0,64 | 0.23 | 2.8 | 1.35 | |
| | | 0,40 | 0.72 | 0,32 | 2,2 | 1,27 | |
| | 9,61 | 0,70 | 0,95 | 0,54 | 1,8 | 1.29 | |
| VI |  | 0,05 | 0,26 | 0,02 | 10.5 | 1,83 | 2,58<br>±0,15 |
| | | 0,07 | 0.36 | 0,04 | 9.8 | 1,83 | |
| | | 0,10 | 0.42 | 0,05 | 7.8 | 1,81 | |
| | | 0,20 | 0.61 | 0,14 | 4,3 | 1,68 | |
| | | 0.30 | 0.68 | 0,17 | 4.0 | 1.64 | |
| | 9.96 | 0.40 | 0.87 | 0.26 | 3.3 | 1.71 | |

TABLE 2. Kinetic Parameters of the Initiated Liquid-Phase Radical Isomerization of 1,3-Dioxacyclanes

| 1,3-Dioxacyclane | $(k_3/\sqrt{k_4})\cdot10^3$ (liter/mole·sec)$^{1/2}$, t = 130°C | $\Delta E_{exp} = \Delta E_3 - 0.5\,\Delta E_4$, kcal/mole | lg $A_3/\sqrt{A_4}$ | $k_3/\sqrt{k_4}$, liter/mole·sec$^{1/2}$ | $\Delta E_3$, kcal/mole |
|---|---|---|---|---|---|
| I | 5,92 | 14.4±0.2 | 5.68 | $4{,}26\cdot10^5\exp(-14400/RT)$ | 14,9 |
| II | 7,00 | 5,4±0,12 | 0.67 | $4{,}67\exp(-5400/RT)$ | 5,9 |
| III | 6,73 | 11.2±0,3 | 3,84 | $6{,}92\cdot10^3\exp(-11200/RT)$ | 11,7 |
| IV | 2.58 | 12.1±0.3 | 3,84 | $6.92\cdot10^3\exp(-12100/RT)$ | 12,6 |



$$DH + \dot{E} \xrightarrow{k_3} \dot{D} + \underset{(EH)}{R(O{=})C{-}O{-}CH_2{-}(CH_2)_n{-}CH_3} \quad (3)$$

$$2\dot{E} \xrightarrow{k_4} \text{molecular products} \quad (4)$$

As seen from a comparison of the $k_3/\sqrt{k_4}$ ratios, at one temperature (130°) the reactivity of 1,3-dioxane ($0.52\cdot10^{-3}$ liter/mole·sec) is lower by factors of 12 and five, respectively, than the reactivities of acetals I and VI. This is evidently determined by the fact that the change in the $sp^3$ hybridization of the $C_2$ atom to $sp^2$ hybridization, which occurs in the rate-determining step of the formation of the cyclic radical [reactions (1) and

TABLE 3. Physicochemical Characteristics of the Starting 1,3-Dioxacyclanes

| Compound | bp, °C | $d_4^{20}$, g/cm³ | $n_D$ (t, °C) |
|---|---|---|---|
| 1,3-Dioxolane (I) | 72,2 | 1,0318 | 1,3887 (25) |
| 2-Methyl-1,3-dioxolane (II) | 81,7 | 1,0231 | 1,3926 (27) |
| 2-Isopropyl-1,3-dioxolane (III) | 122,4 | 0,9802 | 1,4072 (27) |
| 2-Phenyl-1,3-dioxolane (IV) | 106—107 (11) | 0,9784 | 1,5220 (27) |
| 2-Methyl-1,3-dioxane (V) | 109,5 | 0,9890 | 1,4119 (25) |
| 1,3-Dioxepane (VI) | 117,2 | 1,0162 | 1,4319 (25) |

and (3)], is least favorable for the unstrained six-membered ring, whereas the ethyl, propyl, and butyl formate radicals ($\dot{E}$) are identically reactive in the termination processes [reaction (4)]. This is in good agreement with the data on the increased stability of cyclohexane and tetrahydropyran in homolytic reactions as compared with the five-membered analogs [4].

The $k_3/\sqrt{k_4}$ value calculated at 130° for one $C_2$—H bond increases in the series of 1,3-dioxolanes by factors of 2.3, 2.4, and 2.7 on passing from I to 2-isopropyl-, 2-methyl-, and 2-phenyl-1,3-dioxolanes, respectively. This increase in the reactivity of the $C_2$—H bond is determined by stabilization of the resulting cyclic radical ($\dot{D}$) by electron-donor substituents. A similar effect also occurs on passing from 1,3-dioxane to 2-methyl-1,3-dioxane.

On the basis of the above-presented estimates of the effect of substituents, it can be assumed that the primary site of attack by the alkyl radical in the case of unsubstituted or 2-monosubstituted 1,3-dioxacyclanes is the methylene or methylidyne group adjacent to the two heteroatoms, whereas the abilities of all of the remaining C—H bonds to undergo homolytic cleavage are a minimum of one order of magnitude lower.

The experimentally determined activation energies (Table 2) represent the difference between the activation energy of chain propagation ($\Delta E_3$) and half the activation energy of the alkyl radicals in the termination reaction ($\Delta E_4$):

$$\Delta E_3 - 0.5\,\Delta E_4.$$

Like the (E) radicals, ethyl radicals have an activation energy for reaction with one another of $\sim$1.0 kcal/mole [5], and this makes it possible to estimate the $\Delta E_3$ value.

The activation energies obtained are comparable to the activation energy of detachment of hydrogen by peroxy radicals from simple and cyclic ethers [6].

## EXPERIMENTAL

The starting 1,3-dioxacyclanes (I-VI) were obtained by known methods (Table 3) [7, 8]. They were purified by distillation with a sharp rectification column with an efficiency of 30 theoretical plates.

The DTB solutions were prepared in the 1,3-dioxacyclane. In the study of the reaction order with respect to the initiator its concentration was varied from 0.05-1.00 mole/liter in the pure substrate. In the determination of the reaction order with respect to 1,3-dioxacyclane its concentration in benzene was varied from 2.0 moles/liter up to the pure substrate, and the DTB concentration was 0.3 mole/liter. The solutions were placed in glass ampules, and argon was bubbled into them at −10° for 5 min to remove the dissolved oxygen, after which they were hermetically sealed. The start of the reaction was considered to be the time of immersion of the ampules in the thermostat, where a given temperature was maintained with an accuracy of ±0.1°. At definite time intervals, the ampules were removed from the thermostat and cooled. The tert-butyl alcohol and corresponding ester in the cooled reaction mixture were analyzed with an LKhM-72 chromatograph. The typical kinetics of accumulation of the ether are presented in Fig. 3. Preparations I-III and VI were analyzed with a flame-ionization detector. A 4-m-long column with a diameter of 4 mm was used, and the stationary phase was 1,2,3-tri(β-cyanoethoxy)propane on Chromaton NAW.

Isomerization products IV and V were analyzed with a thermal-conductivity detector. A 2-m-long column with a diameter of 4 mm was used; polymethylphenylsiloxane oil on Chromaton NAW served as the phase for V, and polyethylene glycol adipate on Chemosorb served as the phase for IV. Nitrogen was used as the carrier gas when the flame-ionization detector was used; hydrogen was used in the case of the thermal-conductivity detector. The carrier-gas flow rate was 1.5-2.5 liters/h, and the analysis temperature was 60-160°.

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# $^1$H and $^{13}$C NMR SPECTRA AND STRUCTURE OF 2-TRICHLOROMETHYL-4-METHYLENE-1,3-DIOXOLANES

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and T. S. Proskurina

UDC 542.944.547.729.543.422.25

The $^1$H and $^{13}$C NMR spectra of a number of 5-substituted 2-trichloromethyl-4-methylene-1,3-dioxolanes were studied. It was observed that the exocyclic double bond is in effective conjugation with the 3-O ring atom. The configuration of the substituents was established, and a conformational model of these heterocycles of the "envelope" type with the 1-O atom deviating from the plane in which the remaining ring atoms are situated is proposed. The applicability of the $^{13}$C NMR spectra for the determination of the configuration of the compounds is demonstrated.

Continuing our study of the properties of 2-trichloromethyl-4-methylene-1,3-diololanes [1, 2], we have made a more detailed study of their PMR spectra and for the first time have examined the $^{13}$C NMR spectra of a number of representatives of this class of cyclic vinyl ethers in order to obtain information regarding their electronic and three-dimensional structures. The $^1$H and $^{13}$C chemical shifts (CS) for dioxolanes I-VI (the atoms are designated in conformity with the formula presented below) are presented in Table 1. Since the assignment of the signals in the $^1$H and, particularly, the $^{13}$C NMR spectra is not a trivial matter, we will examine this problem in the case of the spectra of I. (See scheme on following page.)

The PMR spectrum of dioxolane I consists of a broad 1-H singlet and a complex multiplet at 4-5 ppm of all of the remaining protons. We were able to analyze the spectrum by using a solvent ($C_6H_6$, 70 mole%) that "simplifies" the PMR spectrum of I and the method of

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